

(19)日本国特許庁 (J P)

(12) 公 開 特 許 公 報 (A)

(11)特許出願公開番号
特開2002-212463
(P2002-212463A)

(43)公開日 平成14年7月31日(2002.7.31)

(51)Int.Cl. ⁷	識別記号	F I	テーマコード*(参考)
C 0 9 D 1/00		C 0 9 D 1/00	4 J 0 3 8
5/16		5/16	5 G 3 0 7
5/24		5/24	
H 0 1 B 5/14		H 0 1 B 5/14	A
13/00	5 0 3	13/00	5 0 3 C
審査請求 未請求 請求項の数13 O L (全 11 頁)			

(21)出願番号 特願2001-4506(P2001-4506)

(22)出願日 平成13年1月12日(2001.1.12)

(71)出願人 501016054
サスティナブル・テクノロジー株式会社
東京都渋谷区代々木五丁目38番6号 オリ
ープビル1階
(72)発明者 緒方 四郎
東京都渋谷区代々木五丁目38番6号 オリ
ープビル1階 サスティナブル・テクノロ
ジー株式会社内
(74)代理人 100108741
弁理士 渡邊 順之

最終頁に続く

(54)【発明の名称】 チタン酸化物含有導電性被膜形成液、該形成液製造方法及びチタン酸化物含有膜を備える構造体

(57)【要約】

【課題】 ガラス、セラミック、金属、プラスチック等の各種基材表面に光触媒性能、抗菌性能、防汚性能、帯電防止能、電磁シールド性等の各種機能を発現させる導電性被膜形成液、該被膜を表面に有する構造体及び該形成液の製造方法の提供。

【解決手段】 塩化銅、硝酸銀、シリカ等の導電性向上物質を、四塩化チタン等の4価チタン塩溶液と塩基性溶液とを反応させてチタン水酸化物を形成する際に混在させ、得られた水酸化物を過酸化水素等の酸化剤でペルオキシ化してアモルファス型過酸化チタン分散液を形成する。また前記分散液を更に加熱することによりしてアナターゼ型に転移させることができる。その結果両型の分散液からなるチタン酸化物含有導電性被膜形成液が製造できる。

【特許請求の範囲】

【請求項1】 導電性向上物質及び超微小粒子のアモルファス型過酸化チタンを含有する分散液からなるチタン酸化物含有導電性被膜形成液。

【請求項2】 アモルファス型過酸化チタン以外の他の超微小粒子の含有量が、アモルファス型過酸化チタン100重量部に対し、100重量部以下である請求項1記載の導電性被膜形成液。

【請求項3】 導電性向上物質及び超微小粒子のアナターゼ型過酸化チタンを含有する分散液からなるチタン酸化物含有導電性被膜形成液。

【請求項4】 分散液が透明である請求項1、2又は3記載の導電性被膜形成液。

【請求項5】 導電性向上物質がシリカゾルである請求項1ないし4のいずれか1に記載の導電性被膜形成液。

【請求項6】 導電性向上物質と、超微小粒子のアモルファス型過酸化チタン及び／又はアナターゼ型過酸化チタンとを含有する導電性被膜を基体表面に有する構造体。

【請求項7】 基体が透光性透明基板である請求項6記載の構造体。

【請求項8】 導電性被膜が光触媒機能又は／及び防汚機能を有する請求項6又は7記載の構造体。

【請求項9】 導電性被膜及び基体が透明である請求項6、7又は8記載の構造体。

【請求項10】 4価チタンの塩溶液と塩基性溶液とを反応させて、チタンの水酸化物を形成し、この水酸化物を酸化剤でペルオキシ化し、これにより超微小粒子のアモルファス型過酸化チタンを形成し、かつこの過程のいずれかにおいて導電性向上物質を添加して導電性向上物質及び超微小粒子のアモルファス型過酸化チタンを含有する分散液を形成することからなるチタン酸化物含有導電性被膜形成液の製造方法。

【請求項11】 4価チタンの塩溶液と塩基性溶液とを反応させて、チタンの水酸化物を形成し、この水酸化物を酸化剤でペルオキシ化し、更に加熱処理することによりアナターゼ型過酸化チタンを転移させ、この過程のいずれかにおいて導電性向上物質を添加して、導電性向上物質及び超微小粒子のアナターゼ型過酸化チタンを含有する分散液を形成することからなるチタン酸化物含有導電性被膜形成液の製造方法。

【請求項12】 導電性向上物質が、4価チタンの塩溶液と塩基性溶液との反応時には混在している請求項10又は11記載の導電性被膜形成液の製造方法。

【請求項13】 請求項10記載の分散液と、請求項11記載の分散液とを混合してアモルファス型過酸化チタンとアナターゼ型過酸化チタンとを含む分散液を形成するチタン酸化物含有導電性被膜形成液の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、板ガラス、タイル等のセラミック、金属板、プラスチック板、タンク、観賞用水槽等の各種基材又は構造物表面に光触媒性能、抗菌性能、防汚性能、防曇性能、帯電防止性能、電磁シールド性等の各種の優れた機能を発現させる薄膜を形成するためのチタン酸化物含有導電性被膜形成液、該導電性被膜を基体表面に有する構造体及び該導電性被膜形成液の製造方法に関する。

【0002】より具体的には、本発明は、特に導電性を向上せしめることができ、その結果先の各種機能をより向上せしめることができる保護膜又は機能膜を形成するためのチタン酸化物含有導電性被膜形成液、該導電性被膜を基体表面に有する構造体及び該導電性被膜形成液の製造方法に関する。また、特に透明性に優れた保護膜又は機能膜を提供することのできるチタン酸化物含有導電性被膜形成液、該導電性被膜を基体表面に有する構造体及び該導電性被膜形成液の製造方法に関する。

【0003】

【従来の技術】チタン含有物質を、板ガラス、白磁器、金属板あるいはタイルなどの建材等の各種材料表面に塗布し、表面汚染防止などの基体表面保護膜、光触媒膜、誘電体膜、半導体膜、紫外線カット膜、着色コーティング膜等の各種性能を有する酸化チタン（チタニア）からなる被膜を形成することが従前から行なわれている。

【0004】その酸化チタン被膜の形成方法としては、酸化チタンの微粒子を含有した分散液あるいはチタン化合物溶液を基体表面に塗布し、塗布した後に乾燥あるいは更に必要に応じ低温焼成する等の方法が知られている。例えば、基体表面にチタンアルコキシドからゾルゲル法により作製した分散液を塗布乾燥する方法、チタンアルコキシドを直接塗布乾燥した後に焼成する方法がある。

【0005】これらの方法では、酸や有機物質を含むので、塗布膜を完成する際には高温に加熱してこれらの有機物質を除去することが必要であり、得られた被膜は不均質あるいは多孔質膜となり易いという問題があった。さらに、チタン含有化合物の水溶液から作製した分散液も常温で放置すると数時間から数日で微粒子がゲル化や凝集が起こり安定性が極めて悪かった。

【0006】そして、それら方法では、酸を含んでいるので塗布できる材料が制限され、焼成の段階で有害なハロゲン化合物を生成する問題もあった。さらに、密着性良好で緻密な膜を形成するには焼成温度は数百度以上を必要とし、プラスチック、金属、低融点ガラスあるいは建材等の材料への利用には制約があった。そこで、このような問題を解決するために、安定で焼成の簡易な、マトリックス成分としてペルオキシポリチタン酸を水等に溶解又は分散した状態で含んだ被膜形成用塗布剤が提案された（特開平7-286114号公報参照）。

【0007】また、低温で比較的密度の高い結晶性のチ

タニア膜を作製することができ、保存安定性もよく、かつ施工者に対する有害性も低い、被膜形成用塗布剤も提案されており（特開平9-71418号公報参照）、その塗布剤は水酸化チタンゲルに過酸化水素水を用いた後に、80℃以上において熱処理してアナターゼからなる酸化チタン微粒子を生成させたものである。この塗布剤は、低温で被膜形成できることから、加熱処理できない材料へのコーティング材料に有用とされている。

【0008】前者の提案された塗布剤は、マトリックス成分としてペルオキソポリチタン酸を水等に溶解した状態あるいは分散した状態で含むものであるが、この塗布液により形成される被膜中のチタン化合物がアナターゼ型の酸化チタンではなく、光触媒活性の発現が期待できないものであり、そのようなことから、被膜形成後のチタン化合物が、触媒活性に優れたアナターゼ型の酸化チタンであることを解決課題とする塗布液も提案された（特開平10-67516号公報）。

【0009】この提案された塗布液は、前記触媒活性以外にも、液体中における分散安定性がよく、塗布後の乾燥、焼成工程が容易で、かつ形成された被膜が緻密であることをも解決課題とするものである。その塗布液は、チタン含有液体から沈殿反応によって形成した水酸化チタン又はチタン酸化物を水中に分散した液に過酸化物を添加してペルオキソチタン溶液にした後に加熱して調製されるものであり、形成された溶液はアナターゼ型の酸化チタンの表面がペルオキソ基で修飾されたものとなっている。

【0010】前述したところの酸化チタン含有被膜及びその被膜形成用溶液は、前述のように各種の特性を持つことから、前記以外にも提案があり、またその後も該被膜形成用溶液及びその関連技術の開発は進められており、それらに伴う各種の提案もある。例えば、アモルファス型過酸化チタンゾルをバインダーとして使用することにより光触媒粒子を基体上に担持固定する光触媒組成物を提供する提案（特開平9-262481号公報）がある。

【0011】さらに、アモルファス型チタン酸化物、特にアモルファス型過酸化チタンゾルが高結合性を有し、かつ耐候性、電磁波遮断性、耐化学薬品性、静電気放電防止性及び防虫性等の各種機能を有することが見出され、それら機能を有する高機能性コーティング剤を提供する提案（特開平10-237352号公報）、あるいはアモルファス型過酸化チタンゾルのコーティング層を撥水性表面に対しても高接着性をもって結合せしめる提案もあり（特開平10-53437号公報）、それはアモルファス型過酸化チタンゾルをコーティング後、常温～250℃未満で乾燥・焼成するものである。

【0012】

【発明が解決しようとする課題】このようなチタン酸化物含有被膜は、各種特性を有する高機能性ものではある

が、現状においては、防汚性能、防曇性能は光不存在での機能発現は十分なものではない。また、電磁波シールドあるいは帯電防止等で求められる導電性に関しても十分なものではなく、これら特性に関しては、更なる向上が望まれている。さらに、それと同時に装飾性及び視覚性能の点からより透明性に優れ、かつ高結合性のものが望まれている。

【0013】本発明者も、チタン酸化物、特に過酸化チタン含有被膜及び該被膜形成用塗布液の有する高機能性及び施工簡便性に着目し、従前より鋭意研究開発に努めており、その結果既に開発した多くの成果を提案している。その後も継続して鋭意研究開発を進めており、その結果、開発に成功したのが、今回提案の発明であり、これにより前述した問題を解消することができた。

【0014】したがって、本発明は、優れた防汚性能、防曇性能と共に電磁波シールド性あるいは帯電防止性に好適な導電性を有し、同時に窓ガラス等に形成する際に求められる装飾性及び視覚性能を発現することのできる透明性を有する高結合性の被膜を提供することのできる、チタン含有導電性被膜形成液、該導電性被膜を基体表面に有する構造体及び該導電性被膜形成液の製造方法を提供することを発明の解決すべき課題とするものである。すなわち、それらのものを提供することを発明の目的とするものである。

【0015】

【課題を解決するための手段】本発明が前記課題を解決するために、チタン酸化物含有導電性被膜形成液、該形成液製造方法及び該導電性被膜を基体表面に有する構造体を提供するものである。そのうちのチタン酸化物含有導電性被膜形成液は、基本的にはアモルファス型過酸化チタンを含有する分散液のものと、アナターゼ型過酸化チタンを含有する分散液ものの2種である。なお、以上のとおりではあるが、両分散液を混合することによりアモルファス型とアナターゼ型の両者が混在するものを形成することも可能である。

【0016】前者のアモルファス型過酸化チタンを含有する分散液からなる導電性被膜形成液は、導電性向上物質及び超微小粒子のアモルファス型過酸化チタンを含有するものであり、後者のアナターゼ型過酸化チタンを含有する分散液からなる導電性被膜形成液は導電性向上物質及び超微小粒子のアナターゼ型過酸化チタンを含有するものである。

【0017】そのチタン酸化物含有導電性被膜形成液の製造方法についても、アモルファス型過酸化チタンを含有する場合と、アナターゼ型過酸化チタンを含有する場合とでは異なっていて、前者の導電性被膜形成液の製造方法は、4価チタンの塩溶液と塩基性溶液とを反応させて、チタンの水酸化物を形成し、この水酸化物を酸化剤でペルオキソ化し、これによりアモルファス型過酸化チタンを形成し、かつこの過程のいずれかにおいて導電性

向上物質を添加して導電性向上物質及び超微小粒子のアモルファス型過酸化チタンを含有する分散液を形成することからなるものである。

【0018】残る後者の導電性被膜形成液の製造方法は、4価チタンの塩溶液と塩基性溶液とを反応させて、チタンの水酸化物を形成し、この水酸化物を酸化剤でペルオキシ化し、更に加熱処理することにより、アナターゼ型過酸化チタンに転移させ、この過程のいずれかにおいて導電性向上物質を添加して、導電性向上物質及び超微小粒子のアナターゼ型過酸化チタンを含有する分散液を形成することからなるものである。

【0019】また、導電性被膜を基体表面に有する構造体は、導電性向上物質と、超微小粒子のアモルファス型過酸化チタン又はアナターゼ型過酸化チタンとを含有する導電性被膜を基体表面に有するものである。その際における導電性被膜にはアモルファス型過酸化チタン又はアナターゼ型過酸化チタンのいずれか一方の単独あるいは両者の共存のいずれでもよい。

【0020】そして、本発明では、チタン酸化物含有導電性被膜形成液により、従前の酸化チタン含有膜形成用溶液より優れた導電性を有する被膜を基体上に形成することができる。そのうちのアモルファス型過酸化チタンを含有する分散液からなるチタン酸化物含有導電性被膜形成液は、透明で、親水性基板のみでなく疎水性基板にも使用可能で良好な結合性能を有する被膜を基体に形成することができる。しかしながら、形成された被膜は疎水性で、チタニアの光触媒能がない。そのため被膜形成された基体は光触媒による劣化が回避できるという特色がある。

【0021】また、アナターゼ型過酸化チタンを含有する分散液からなるチタン酸化物含有導電性被膜形成液は、透明で、親水性の被膜を形成する。その形成された被膜は触媒能を有し、かつ安定性に優れ強固な結合力を有するものである。そのため導電性、防汚性能及び防曇性能を有すると同時に透明性に優れた被膜が形成でき、その結果窓ガラス等の視覚性能を求められる基体を使用する際に特に好適である。

【0022】

【発明の実施の形態】本発明は、前述したとおりチタン酸化物含有被膜形成液、該形成液製造方法及びチタン酸化物含有被膜を備える構造体の発明であり、チタン酸化物含有被膜形成液は、基本的にはアモルファス型過酸化チタン含有のものと、アナターゼ型過酸化チタン含有のものの2種であり、前者は、4価チタンの塩溶液と塩基性溶液とを反応させて、チタンの水酸化物を形成し、この水酸化物を過酸化水素等の酸化剤でペルオキシ化し、アモルファス型過酸化チタンを形成し、かつこの過程のいずれかにおいて導電性向上物質を添加することにより製造される。

【0023】また、後者のアナターゼ型過酸化チタンを

含有するチタン酸化物含有被膜形成液は、4価チタンの塩溶液と塩基性溶液とを反応させて、チタンの水酸化物を形成し、この水酸化物を酸化剤でペルオキシ化し、更に加熱処理することにより、アナターゼ型過酸化チタンに転移させ、この過程のいずれかにおいて導電性向上物質を添加することにより製造される。なお、前記したとおりの本発明のチタン酸化物含有被膜形成液は、基本的には2種であるが、両分散液を混合することによりアモルファス型とアナターゼ型の両者が混在するものを形成することも可能であり、混合比率の調節することにより各種比率のアモルファス型とアナターゼ型の比率は自由に選択できる。

【0024】本発明のチタン酸化物含有被膜形成液製造の際に使用する4価チタンの塩溶液としては、アンモニア水、苛性ソーダ溶液等の塩基性溶液と反応させた際にオルトチタン酸(H_4TiO_4)とも呼称される水酸化チタンのゲルを形成できるものであれば各種のチタン化合物が使用でき、それには例えば、4塩化チタン、硫酸チタン、硝酸チタンあるいはリン酸チタン等のチタンの水溶性無機酸塩がある。それ以外にも蔞酸チタン等の水溶性有機酸塩も例示できる。なお、これらの各種チタン化合物の中では、製造された被膜形成液中にチタン化合物中のチタン以外の成分が残留しない点で4塩化チタンが好ましい。

【0025】また、これらの4価チタンの塩溶液と反応させる塩基性溶液は、4価チタンの塩溶液と反応して水酸化チタンのゲルを形成できるものであれば、各種のものが使用可能であり、それには例えばアンモニア水、苛性ソーダ溶液、炭酸ソーダ溶液あるいは苛性カリ溶液等が例示できるが、アンモニア水が好ましい。その後形成された水酸化チタンを酸化する酸化剤としては、酸化後ペルオキシ化物が形成できるものであれば各種の酸化剤が制限なく使用できるが、製造された被膜形成液中に、金属イオンあるいは酸イオン等の残留物の生じない過酸化水素が望ましい。

【0026】4価チタンの塩溶液及び塩基性溶液の両溶液の濃度については、反応時の濃度が、水酸化チタンのゲルが形成できる範囲であれば特に制限されるものではないものの比較的希薄な溶液がよい。具体的には、4価チタン塩溶液は5～0.01wt%がよく、好ましくは0.9～0.3wt%がよい。また、塩基性溶液は10～0.5wt%がよく、好ましくは4.0～2.0wt%がよい。特に塩基性溶液にアンモニアを使用した場合の濃度は、前記した範囲の10～0.5wt%がよく、好ましくは4.0～2.0wt%がよい。

【0027】導電性向上物質としては、チタン酸化物単独含有の被膜形成液により形成される被膜に比し、導電性を向上せしめることができるものであれば、金属塩等の各種物質が使用可能である。金属塩としては、例えば、アルミニウム、錫、クロム、ニッケル、アンチモ

ン、鉄、銀、セシウム、インジウム、セリウム、セレン、銅、マンガン、カルシウム、白金、タングステン、ジルコニウム、亜鉛等の金属塩があり、それ以外にも一部の金属あるいは非金属等については水酸化物あるいは酸化物も使用可能である。

【0028】それらについてより具体的に物質名で示すと、塩化アルミニウム、塩化第1及び第2錫、塩化クロム、塩化ニッケル、塩化第1及び第2アンチモン、塩化第1及び第2鉄、硝酸銀、塩化セシウム、三塩化インジウム、塩化第1セリウム、四塩化セレン、塩化第2銅、塩化マンガン、塩化カルシウム、塩化第2白金、四塩化タングステン、オキシ二塩化タングステン、タングステン酸カリウム、塩化第2金、オキシ塩化ジルコニウム、塩化亜鉛等の各種の金属塩が例示できる。また、金属塩以外の化合物としては、水酸化インジウム、ケイタングステン酸、シリカゾル、水酸化カルシウム等が例示できる。

【0029】本発明の導電性被膜形成液の製造に当たっては、まず、4価チタンの塩溶液と塩基性溶液とを反応させて、水酸化チタンゲルを形成することになる。その際の反応液の濃度及び温度については、特に限定されるわけではないが、希薄溶液及び常温で実施するのが好ましい。この反応は中和反応であり、酸性から中性、すなわちpH7になることが確認できるまで行うのが望ましい。その反応後は形成された水酸化チタンゲルを重量沈降あるいは遠心分離等により固液分離し、分離後同ゲルを水洗するのが好ましい。

【0030】本発明で使用する導電性向上物質は、4価チタンの塩溶液と塩基性溶液とを反応させて水酸化チタンを形成する際に共存させるのが望ましく、そのためには水酸化物形成反応前に4価チタンの塩溶液中に添加等により存在させるか、該反応時に反応系に添加するのが好ましい。このようにすることにより添加される導電性向上物質によっては水酸化物形成反応時に水酸化チタンと同様に水酸化物が形成されて共沈することができる。

【0031】前記のようにして得られた水酸化チタンは、それに過酸化水素等の酸化剤を添加しペルオキシ化することにより導電性を有する超微小粒子のアモルファス型過酸化チタンが形成される。その粒子の粒径は2nm～20nmであり、より透明度が高く好ましい状態の被膜形成液の場合には10nm以下である。得られたアモルファス型過酸化チタンを含有する導電性被膜形成液により形成した被膜は、疎水性であり、親水性の基体ばかりでなく疎水性基体にも固着力に優れた被膜を形成することができる。

【0032】また、形成される被膜には触媒性能はなく、そのため光による基体の酸化劣化が回避できる。なお、その形成液においては、アモルファス型過酸化チタンと、それ以外の超微小粒子との含有量の比率は、アモルファス型過酸化チタン100重量部に対し、100重

量部以下であることが望ましく、これにより安定した疎水性膜形成用の導電性被膜形成液が得られる。

【0033】これに対して、アナターゼ型過酸化チタンを含有する導電性被膜形成液は、前記で形成された超微小粒子のアモルファス型過酸化チタン溶液を加熱することにより形成されるが、その加熱温度は80～200℃がよく、特に大気圧下での加熱が簡便で好ましく、このようにして得られた被膜形成液は透明性が高く、その結果形成された被膜は透明度が高く、視界性能あるいは装飾性能を求められる用途には好適である。また暗所でも親水性を呈する。

【0034】特にアナターゼ型過酸化チタンを含有する分散液からなるチタン酸化物含有導電性被膜形成液を製造する場合には、導電性向上化合物と4価チタンの塩溶液とを塩基性溶液との反応時に両者とも水酸化物として共沈させ、その後チタン酸化物を酸化してペルオキシ化し、ついで加熱してアナターゼ型に転移させることにより透明性の高い分散液が形成でき、これを使用して導電性被膜を形成した場合には透明性の高い親水性被膜が形成でき、その結果視界性能あるいは装飾性が重要視される建築物の窓ガラスや光学ガラスあるいはプラスチック板等の透光性透明基板には好適である。

【0035】以下において、本発明の導電性被膜形成液の製造方法の実施の形態について、図面に基づいて好ましい態様を中心にしてより詳細に説明する。本発明の導電性被膜形成液は、前述したとおり基本的にはアモルファス型過酸化チタンを含有するものと、アナターゼ型過酸化チタンを含有するもの2種があるが、まず前者の導電性被膜形成液の製造方法から図1に基づいて説明する。

【0036】前者のアモルファス型過酸化チタンを含有するものを製造するに当たっては、まず、高濃度の四塩化チタン溶液及びアンモニア水を希釈する。希釈は希釈後の濃度がそれぞれ5.0～0.01重量%及び10.0～0.5重量%になるように行なうのがよく、好ましくはそれぞれ0.7～0.3重量%及び4.0～2.0重量%になるようにするのがよい。

【0037】希釈後両溶液を混合して水酸化チタンゲルを形成するが、その反応時には導電性向上物質が反応系中に共存するのがよく、そのために前記混合を行なう前に四塩化チタン溶液中に導電性向上物質を混合しておくのがよい。導電性向上物質は前記したとおり各種のものが使用できるが、好ましくは塩化銅、第1、第2塩化錫あるいは第1、第2塩化鉄等がよい。なお、前記した時点で導電性向上物質を混入させた場合には、混入される導電性向上物質によっては水酸化物形成反応時に水酸化チタンと同様に水酸化物が形成されて共沈することができる。

【0038】チタン酸化物形成反応の反応液温度については、特に限定されるわけではないが、常温で実施する

のが好ましい。この反応は中和反応であり、酸性から中性、すなわちpH7になることが確認できる程度まで行うのが望ましい。その反応後は形成された水酸化チタンゲルを重力沈降あるいは遠心分離等により固液分離し、分離後同ゲルから共存する塩素イオン等の陰イオンを除去するために水洗するのが好ましい。

【0039】ついで、酸化剤により酸化チタンをペルオキシ化することになるが、その前に冷却するのが好ましい。その際の冷却は水酸化チタンが1～5℃になるように行うのがよい。ペルオキシ化する際の酸化剤としては、過酸化水素が望ましく、その濃度は特に制限されることはないが、30～40%のものがよい。なお、酸化剤については、過酸化水素に制限されるものではなく、前述したとおりペルオキシ化物、すなわち過酸化チタンが形成できるものであれば各種のものが使用できる。

【0040】前記のように酸化チタンと過酸化水素とを混合することによりペルオキシ化反応が次第に進行し、アモルファス型過酸化チタンが形成されるが、粒径が小さく、透明性の優れた分散液を得るには、前記反応は短時間で低温で行うのがよい。得られた分散液が本発明でいうところの導電性被膜形成液であり、これに対して限外濾過を行なうことにより水分を分離し濃度を高めることができる。得られた被膜形成液は通常黄色であるが、使用した導電性向上物質によっては、その影響を受け、緑あるいは青等のものとなる。なお、透明性の優れた分散液を得るには、超微小粒子の粒径は、ほぼ2nm～20nmがよく、10nm以下の場合には透明度の高いものとなり望ましい。

【0041】前述の通り、このアモルファス型過酸化チタン含有分散液によりなる被膜形成液から得られる被膜は疎水性であり、その結果、親水性基体のみでなく、疎水性基体にも強固着力の被膜を形成することができる。また、その被膜には触媒性能がなく、そのため光による基体の酸化劣化が回避できる。なお、その形成液においては、アモルファス型過酸化チタンと、それ以外の超微小粒子との含有量の比率は、アモルファス型過酸化チタン100重量部に対し、100重量部以下であることが望ましく、これにより安定した疎水性被膜形成用の導電性被膜形成液が得られる。

【0042】以上はアモルファス型過酸化チタンを含有する被膜形成液の製造方法についてであるが、以下において、アナターゼ型過酸化チタンを含有する導電性被膜形成液の製造方法について説明する。前記のアモルファス型過酸化チタン分散液を加熱することにより、過酸化チタンがアモルファス型からアナターゼ型に転移しアナターゼ型過酸化チタン分散液が形成され、その結果アナターゼ型過酸化チタンを含有する導電性被膜形成液が製造できる。その際の加熱温度は80～200℃でよく、好ましくは90～120℃がよい。また、その加熱は、電気あるいは燃焼熱によるだけでも可能ではあるが、こ

れらに電磁波による加熱を併用し、可能な限り加熱時間を短縮するのがよい。

【0043】前記併用加熱を採用した場合にはアモルファス型からアナターゼ型への転移が短縮できると共に超微小粒子の粒径の成長や凝集を抑制することができ、かつペルオキシ基の減少及びH₂Oとの反発力（ゼーター電位）を弱めることもない透明分散液ができる。このようにして得られるアナターゼ型過酸化チタンの超微小粒子の粒径は2～20nmがよく、望ましくは10nm以下がよい。なお、前述の製造方法によりアモルファス型とアナターゼ型過酸化チタンの2種の分散液がそれぞれ製造できるが、それを単独で使用するだけでなく、両分散液を混合することにより両者が任意の比率の分散液を形成することもできる。

【0044】本発明のチタン酸化物含有導電性被膜形成液の製造方法における導電性向上物質の添加時期については、前述のとおり四塩化チタン等の4価チタンの塩溶液と塩基性溶液との反応前又は反応時が好ましく、これにより透明度、導電性、固着性等の各種特性に関し優れたものが得られることも前述のとおりである。しかしながら、前記製造プロセスのそれ以外の時期に導電性向上物質を混入しても導電性被膜形成液は製造できるのであり、その混入時期としては水洗前の固液分離後の沈殿物ゲル生成時、ペルオキシ化反応後に行う限外濾過後の濃度調整被膜形成液製造時あるいはアナターゼ型転移後に行う限外濾過後の濃度調整被膜形成液製造時等がある。

【0045】本発明の導電性被膜形成液の使用対象物としては、光触媒性能、抗菌性能、防汚性能、防曇性能、帯電防止能、電磁シールド性等の各種機能が要求される各種材料あるいは構造物が該当する。それら材料としては、板ガラス、セラミック、ステンレス、アルミ等の金属板、アクリル、ポリカーボネート、PET等のプラスチック板、綿布あるいは繊維等が例示できる。

【0046】また、構造物としては、建築物、自動車等の窓ガラス、自動車等の車両外装材、タンク、観賞用等の各種水槽、金属、プラスチック等のパイプ、衛生陶器、眼鏡、レンズ、レンズフィルター、貯湯器、浴槽機器、洗面機器、流し台、ドア取手、水道用活栓、道路用ミラー、電磁シールド材、基板等の半導体材料、複写機内部部品等の各種ものが例示できる。

【0047】本発明の被膜形成液により形成された被膜は、前述したとおり導電性に優れており、その結果光触媒性能が発揮しがたい金属、プラスチック等のパイプ内面に被膜を形成された場合においても、軟質もしくは硬質スケール、スライム又は鉄錆等の汚染物がパイプ内面に形成もしくは付着しにくく、防汚性能に優れている。特に水道管に使用した場合には、スケール、スライム又は錆びが発生し難く好適である。

【0048】それに加えて、特にアモルファス型過酸化チタン分散液の被膜形成液の場合は、形成被膜には光触

10

20

30

40

50

媒能がないが、そのために基体がプラスチックの場合には、かえって太陽光による分解の危惧もなく特色となる。またアナターゼ型過酸化チタンの分散液の被膜形成液の場合には、形成被膜は耐久性、結合性に優れ、かつ透明性も優れているので、窓ガラス、又はアクリル、ポリカーボネート、PET等の透明プラスチック板もしくは容器の場合には、視覚性能に優れていると共に防汚性能及び防曇性能も優れている。

【0049】

【実施例】以下に、本発明の被膜形成液の製造及び該形成液を使用する導電性被膜の製造に関する実施例を記載する。また、合わせて形成した被膜について導電性試験、親水性試験及び防汚性能試験を行い、それらの手順及び結果に関し記載するが、本発明はこれらの例及び試験によって何等限定されるものではなく、特許請求の範囲の記載によって特定されるものであることはいうまでもない。なお、被膜形成液製造実施例及び導電性被膜製造実施例に関しては、以下においては、それぞれ製造例及び被膜形成例と呼称する。

【0050】[製造例1]純水500mlに純度97%CuCl₂・2H₂O（日本化学産業(株)製）0.463gを完全に溶かした溶液に、更に50%四塩化チタン溶液（住友シチックス(株)製）10gを添加し純水を加え1000mlにした溶液を準備する。これに25%アンモニア水（高杉製薬(株)製）を10倍希釈したアンモニア水を滴下してpH6.9に調整して水酸化銅と水酸化チタンとの混合物を沈殿させた。

【0051】この沈殿物を純水で上澄み液中の導電率が0.8mS/m以下になるまで洗浄を継続し、導電率が0.782mS/mになったところで洗浄を終了すると、0.96wt%濃度の水酸化物の含有液が350g作製された。次いで、この含有液を1～5℃に冷却しながら35%過酸化水素（タイキ薬品工業(株)製）を25g添加し16時間攪拌すると青緑色の透明な銅がドーブされた0.96wt%濃度のアモルファス型過酸化チタンの分散液370gが得られた。

【0052】この得られたアモルファス型過酸化チタン分散液を100g秤量し100℃で5時間加熱すると更に青みが増し強い青緑色の銅がドーブされたアナターゼ型過酸化チタンゾルが1.6wt%濃度のアナターゼ型過酸化チタン分散液60gが得られた。これを純水で希釈して造膜塗布用の0.85wt%アナターゼ型過酸化チタン分散液112gに調製した。残りのアモルファス型過酸化チタンの分散液270gは、純水で希釈して0.85wt%のアモルファス型過酸化チタンの分散液304gを調製した。

【0053】[製造例2]後記する比較製造例における0.85wt%のアナターゼ型過酸化チタン分散液60gに対し、硝酸銀を濃度0.005mol/lになるように0.050g添加し、銀がドーブされたアナターゼ

型過酸化チタン分散液を調製した。

【0054】[製造例3]前記製造例1で調製された銅がドーブされた、0.85wt%のアナターゼ型過酸化チタンの分散液67gに対し、硝酸銀を濃度0.005mol/lになるように0.057g添加し、銀及び銅がドーブされたアナターゼ型過酸化チタンの分散液を調製した。

【0055】[製造例4]純水500gに純度97%CuCl₂・2H₂O（日本化学産業(株)製）0.463gを完全に溶かした溶液に、更に30wt%シリカゾル2.5gと50wt%四塩化チタン溶液（住友シチックス(株)製）10gを添加し純水を加え1000gにした溶液を準備する。これに25%アンモニア水（高杉製薬(株)製）を10倍希釈したアンモニア水を滴下してpH6.9に調整して水酸化銅と水酸化チタンとの混合物を沈殿させた。

【0056】この沈殿物を純水で上澄み液中の導電率が0.8mS/m以下になるまで洗浄を継続し、導電率が0.688mS/mになったところで洗浄を終了すると、0.96wt%濃度の水酸化物の含有液が345g作製された。次いで、この含有液を1～5℃に冷却しながら35%過酸化水素（タイキ薬品工業(株)製）を25g添加し16時間攪拌すると青緑色の透明な銅とシリカがドーブされた1.05wt%濃度のアモルファス型過酸化チタンの分散液370gが得られた。

【0057】この得られたアモルファス型過酸化チタン分散液を100g秤量し100℃で5時間加熱すると銅とシリカがドーブされたアモルファス型過酸化チタンの分散液より青みの強い緑青色の透明な銅とシリカがドーブされたアナターゼ型過酸化チタンゾルが1.72wt%濃度で60g得られた。これを純水で希釈して造膜塗布用の0.85wt%アナターゼ型過酸化チタン分散液120gに調製した。

【0058】[比較製造例]純水500gに50wt%四塩化チタン溶液（住友シチックス(株)製）10gを添加し純水を加え1000gにした溶液を準備する。これに25%アンモニア水（高杉製薬(株)製）を10倍希釈したアンモニア水を滴下してpH6.9に調整し水酸化チタンを沈殿させた。この沈殿物を純水で上澄み液中の導電率が0.8mS/m以下になるまで洗浄を継続し、導電率が0.738mS/mになったところで洗浄を終了すると、0.73wt%濃度の水酸化物の含有液が430g作製された。

【0059】次いで、この含有液を1～5℃に冷却しながら35%過酸化水素（タイキ薬品工業(株)製）を25g添加し16時間攪拌すると淡黄褐色0.86wt%濃度のアモルファス型過酸化チタンの分散液450gが得られた。この得られたアモルファス型過酸化チタン分散液を100g秤量し100℃で5時間加熱すると淡黄色のアナターゼ型過酸化チタン分散液が1.52wt%濃

度で55g得られた。これを純水で希釈して造膜塗布用の0.85wt%アナターゼ型過酸化チタン分散液98gに調製した。

【0060】[製造例5]純水500mlに $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (塩化第二鉄) 0.712gを完全に溶かした溶液に、更に50%四塩化チタン溶液(住友シチックス(株)製)10gを添加し純水を加え1000mlにした溶液を準備する。これに25%アンモニア水(高杉製薬(株)製)を10倍希釈したアンモニア水を滴下してpH7.1に調整して水酸化鉄と水酸化チタンとの混合物を沈殿させた。この沈殿物を純水で上澄み液中の導電率が0.8mS/m以下になるまで洗浄を継続し、導電率が0.744mS/mになったところで洗浄を終了すると、0.47wt%濃度の水酸化物の含有液が420g作製された。

【0061】次いで、この含有液を1~5℃に冷却しながら35%過酸化水素(タイキ薬品工業(株)製)を25g添加し16時間攪拌すると濃黄褐色の透明な鉄がドーブされたアモルファス型過酸化チタンの分散液440gが得れた。得られたアモルファス型過酸化チタン分散液を100g秤量し100℃で5時間加熱すると淡黄色の鉄がドーブされたアナターゼ型過酸化チタンゾルが1.1wt%濃度のアナターゼ型過酸化チタン分散液48gが得られた。

【0062】[製造例6]純水500mlに $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (塩化第一錫) 0.594gを完全に溶かした溶液に、更に50%四塩化チタン溶液(住友シチックス(株)製)10gを添加し純水を加え1000mlにした溶液を準備する。これに25%アンモニア水(高杉製薬(株)製)を10倍希釈したアンモニア水を滴下してpH7.0に調整して水酸化錫と水酸化チタンとの混合物を沈殿させた。この沈殿物を純水で上澄み液中の導電率が0.8mS/m以下になるまで洗浄を継続し、導電率が0.713mS/mになったところで洗浄を終了すると、0.51wt%濃度の水酸化物の含有液が417g作製された。

【0063】次いで、この含有液を1~5℃に冷却しながら35%過酸化水素(タイキ薬品工業(株)製)を25g添加し16時間攪拌すると黄褐色の透明な錫がドーブされたアモルファス型過酸化チタンの分散液439gが得れた。得られたアモルファス型過酸化チタン分散液を100g秤量し100℃で5時間加熱すると淡黄色の錫がドーブされたアナターゼ型過酸化チタンゾルが1.02wt%濃度のアナターゼ型過酸化チタン分散液48gが得られた。

【0064】[製造例7]純水500mlに ZnCl_2 (塩化亜鉛) 0.359gを完全に溶かした溶液に、更に50%四塩化チタン溶液(住友シチックス(株)製)10gを添加し純水を加え1000mlにした溶液を準備する。これに25%アンモニア水(高杉製薬(株)製)

を10倍希釈したアンモニア水を滴下してpH7.0に調整して水酸化亜鉛と水酸化チタンとの混合物を沈殿させた。この沈殿物を純水で上澄み液中の導電率が0.8mS/m以下になるまで洗浄を継続し、導電率が0.713mS/mになったところで洗浄を終了すると、0.48wt%濃度の水酸化物の含有液が409g作製された。

【0065】次いで、この含有液を1~5℃に冷却しながら35%過酸化水素(タイキ薬品工業(株)製)を25g添加し16時間攪拌すると黄褐色の透明な亜鉛がドーブされたアモルファス型過酸化チタンの分散液430gが得れた。得られたアモルファス型過酸化チタン分散液を100g秤量し100℃で5時間加熱すると淡黄色の亜鉛がドーブされたアナターゼ型過酸化チタンゾルが0.96wt%濃度のアナターゼ型過酸化チタン分散液48gが得られた。

【0066】[製造例8]純水500mlに $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (塩化ニッケル) 0.594gを完全に溶かした溶液に、更に50%四塩化チタン溶液(住友シチックス(株)製)10gを添加し純水を加え1000mlにした溶液を準備する。これに25%アンモニア水(高杉製薬(株)製)を10倍希釈したアンモニア水を滴下してpH7.0に調整して水酸化ニッケルと水酸化チタンとの混合物を沈殿させた。この沈殿物を純水で上澄み液中の導電率が0.8mS/m以下になるまで洗浄を継続し、導電率が0.679mS/mになったところで洗浄を終了すると、0.71wt%濃度の水酸化物の含有液が403g作製された。

【0067】次いで、この含有液を1~5℃に冷却しながら35%過酸化水素(タイキ薬品工業(株)製)を25g添加し16時間攪拌すると濃黄褐色の透明なニッケルがドーブされたアモルファス型過酸化チタンの分散液425gが得れた。得られたアモルファス型過酸化チタン分散液を100g秤量し100℃で5時間加熱すると淡黄褐色のニッケルがドーブされたアナターゼ型過酸化チタンゾルが1.30wt%濃度のアナターゼ型過酸化チタン分散液48gが得られた。

【0068】[製造例9]純水500mlに純度97% $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (日本化学産業(株)製) 0.230gと $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (塩化第二鉄) 0.351gを完全に溶かした溶液に、更に50%四塩化チタン溶液(住友シチックス(株)製)10gを添加し純水を加え1000mlにした溶液を準備する。これに25%アンモニア水(高杉製薬(株)製)を10倍希釈したアンモニア水を滴下してpH7.0に調整して水酸化銅と水酸化鉄と水酸化チタンとの混合物を沈殿させた。この沈殿物を純水で上澄み液中の導電率が0.8mS/m以下になるまで洗浄を継続し、導電率が0.779mS/mになったところで洗浄を終了すると、0.76wt%濃度の水酸化物の含有液が398g作製された。

【0069】次いで、この含有液を1～5℃に冷却しながら35%過酸化水素(タイキ薬品工業(株)製)を25g添加し16時間攪拌すると青緑色の透明な銅と鉄がドーブされたアモルファス型過酸化チタンの分散液420gが得れた。得られたアモルファス型過酸化チタン分散液を100g秤量し100℃で5時間加熱すると緑青色の銅と鉄がドーブされたアナターゼ型過酸化チタンゾルが1.42wt%濃度のアナターゼ型過酸化チタン分散液45gが得られた。

【0070】[被膜形成例1ないし4及び被膜形成比較例]製造例1, 4及び比較製造例で製造したアモルファス型、並びに製造例2, 3で製造したアナターゼ型過酸化チタンの分散液を用いて、10×10cmの磁器タイル表面に塗膜を形成した。塗膜形成後100℃で15分間加熱して、導電性及び親水性試験用のタイルを調製した。

【0071】[導電性試験]導電性は、表面抵抗測定装置(ロレスタAP、三菱化学社製)を使用し、前記で調製したタイルについて二点間の表面抵抗を測定した。この測定値が低い場合は導電性に優れていることを示している。したがって、高い場合には導電性が劣ることになる。

【0072】[親水性試験]親水性は、接触角計(CAX型、協和界面科学(株)製)を使用し、前記で調製したタイルについて、調整後40時間暗所に放置した後、以下のとおりの手順で親水角度を測定した。なお、この測定値が10～40°未満の場合には親水性であり、40*

*～80°の場合には疎水性である。

【0073】それら測定結果は表1に示すとおりである。この結果によれば、導電性向上物質が混入されていない比較製造例の過酸化チタン含有分散液を用いて調製されたタイルの表面抵抗が実施例である製造例のそれに比し3桁以上表面抵抗が大きく、導電性が低いことがわかる。

【0074】また、この表から、導電性向上物質が混入された本発明の被膜形成液においては、過酸化チタンがアモルファス型の場合よりも、アナターゼ型の場合の方が導電性に優れていることもわかる。さらに、混入する導電性向上物質については、金属化合物のみの場合よりもシリカが混在している場合の方が導電性に優れていることもわかる。

【0075】そして、親水性については、同様に表1からアモルファス型分散液による被膜の場合の方が、アナターゼ型分散液による被膜の場合に比し、親水角度が大きく、疎水性であることがわかる。特に銅化合物が混入されている場合には、導電性向上物質無混入の比較製造例の形成液を使用した場合の2倍以上の親水角度となっており、超親水性である。また、導電性向上化合物としてシリカが金属化合物と共に混入している場合には、金属化合物のみの場合よりも親水角度が小さく、超親水性である。

【0076】

【表1】

試験例番号	使用分散液	導電性(Ω/□)	親水性
被膜形成例1	製造例1 (アモルファス型)	4.0×10^4	85°
被膜形成例2	製造例2 (アナターゼ型)	5.6×10^5	10°
被膜形成例3	製造例3 (アナターゼ型)	3.2×10^5	8°
被膜形成例4	製造例4 (アモルファス型)	2.1×10^4	15°
被膜形成比較例	比較製造例 (アモルファス型)	3.0×10^7	42°

【0077】[防汚性能評価]まず、防汚性能評価用導電性被膜形成液を以下のとおり調製した。

[製造例10]前記製造例4における銅とシリカがドーブされた0.85wt%のアナターゼ型分散液60gを採取し、これに対し硝酸銀を0.005mol/lになるように0.050g添加し、銅、銀及びシリカがドーブされたアナターゼ型過酸化チタン分散液を調製した。 ※50

※【0078】[製造例11]製造例1で得た銅がドーブされた0.85wt%のアモルファス型過酸化チタン分散液と、銅がドーブされた0.85wt%のアナターゼ型過酸化チタン分散液とを、3:7の割合で混合し混合液を60g調製した。この混合液に対し、硝酸銀を濃度0.005mol/lになるように0.050g添加し、銅及び銀がドーブされたチタン酸化物含有導電性被

膜形成液を調製した。

【0079】[防汚性能評価用試料の調製]製造例10で調製した、銀化合物、銅化合物及びシリカを混入するアナターゼ型過酸化チタンを含有する分散液からなるチタン酸化物含有導電性被膜形成液を内径100mm、長さ200mmのステンレスパイプ(SUS 304)の内面に造膜し、乾燥後250℃で15分間加熱し、導電性被膜を形成した。また、比較のために導電性被膜形成液を形成していない同様のステンレスパイプも用意した(比較例1)

【0080】製造例11で調製した導電性被膜形成液を塗膜量が0.8g/cm²となるようにアクリル樹脂板(70×120mm)にスプレー吹付けし、乾燥後80℃で15分間加熱して、導電性被膜を形成した。また、比較のために導電性被膜形成液を形成していない同様の樹脂板も用意した(比較例2)

【0081】[防汚性能試験]前記で製造したパイプ及び樹脂板、それに加えて比較用の導電性被膜を形成していないパイプ及び樹脂板を容積20リットル(1)のポリ容器に101の河川水と共に入れ、暗所で保存し、1ヶ月及び2ヶ月後に取り出して目視にて表面の汚染状態を観察した。その結果は表2に示す通りである。

【0082】[汚染状態評価基準]汚染状態の評価基準は、表面に付着した汚れにより以下の通り評価した。

○：ほとんど付着がない。

△：やや付着がある。

×：付着が明確である。

【0083】汚染状態の評価結果は表2に示す通りである。その結果によれば、導電性被膜が表面に形成されている実施例のパイプ及び樹脂板は、それが形成されていない比較例のものに比し、汚れの付着がなく、防汚性に優れていることが明白である。また、混入された導電性向上物質に一部差異はあるものの、過酸化チタンについては、アモルファス型とアナターゼ型が混在している場合よりも、アナターゼ型単独の場合の方が防汚性能が優れている。

【0084】

【表2】

使用分散液	試験期間	
	1ヶ月	2ヶ月
製造例10	○	○
比較例1	△	×
製造例11	○	△
比較例2	△	×

【0085】

【発明の効果】本発明のチタン酸化物含有導電性被膜形成液は、従前の酸化チタン含有膜形成用溶液より優れた導電性を有する被膜を板ガラス、タイル等のセラミック、金属板、プラスチック板等の各種の基体表面に形成することができる。この被膜により微生物等の有害物分解能を有する光触媒性能、抗菌性能、タイルあるいはガラス表面等の防汚性能、防曇性能、複写機内等の帯電防止性能、電磁シールド性等の各種の優れた機能を発現させることができる。

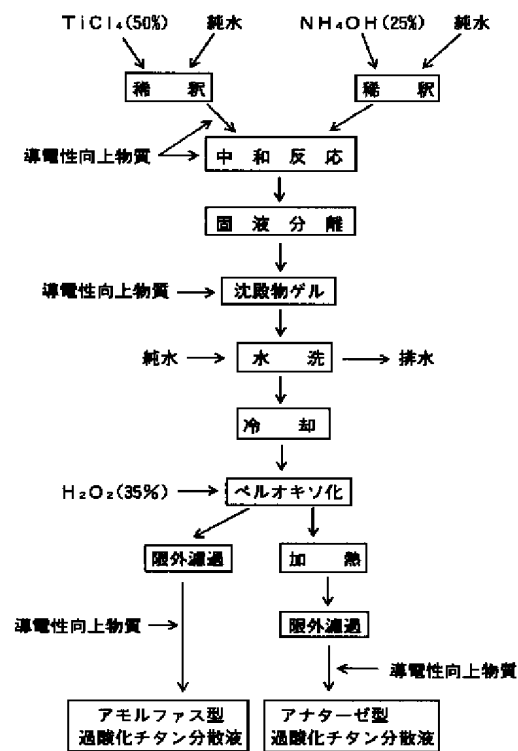
【0086】中でも、導電性を特に向上せしめることができるから、それに関連した機能には好影響を与えることができる。例えばイオン化した物質が付着し難くなる。このような特性を有する導電性被膜形成液のうち、アモルファス型過酸化チタン含有分散液から形成された被膜は疎水性で光触媒能がない。そのため親水性基体のみでなく、疎水性基体にも優れた結合性を有する被膜を形成でき、かつ被膜形成基体は光触媒による劣化が回避できるという特色がある。

【0087】また、アナターゼ型過酸化チタン含有分散液からなるチタン酸化物含有導電性被膜形成液は透明で、形成された被膜は親水性で、光触媒能を有し、かつ安定性、結合性にも優れている。そのため導電性、防汚性能及び防曇性能を有すると同時に透明性に優れた被膜が安定かつ強結合で形成でき、その結果窓ガラス等の視覚性能を求められる基体に使用する際に好適である。

【図面の簡単な説明】

【図1】本発明の導電性被膜形成液の製造方法の概要を示す図。

【図1】



フロントページの続き

(72)発明者 松井 義光
佐賀県藤津郡嬉野町大字岩屋川内甲476番
地 サスティナブル・テクノロジー株式会
社佐賀研究所内

Fターム(参考) 4J038 AA011 HA211 HA241 HA441
NA01 NA05 NA20 PB02 PB05
PB06 PB07 PB09 PC02 PC03
PC08
5G307 FA01 FA02 FB01 FC09

PAT-NO: JP02002212463A
DOCUMENT-IDENTIFIER: JP 2002212463 A
TITLE: TITANIUM OXIDE-CONTAINING
CONDUCTIVE FILM-FORMING LIQUID,
PRODUCTION METHOD THEREOF, AND
STRUCTURE EQUIPPED WITH TITANIUM
OXIDE-CONTAINING FILM
PUBN-DATE: July 31, 2002

INVENTOR-INFORMATION:

NAME	COUNTRY
OGATA, SHIRO	N/A
MATSUI, YOSHIMITSU	N/A

ASSIGNEE-INFORMATION:

NAME	COUNTRY
SUSTAINABLE TITANIA TECHNOLOGY INC	N/A

APPL-NO: JP2001004506
APPL-DATE: January 12, 2001

INT-CL (IPC): C09D001/00 , C09D005/16 , C09D005/24 , H01B005/14 ,
H01B013/00

ABSTRACT:

PROBLEM TO BE SOLVED: To provide an electroconductive film-forming liquid which imparts various functions, such as photocatalytic, antibacterial, stainproof, antistatic, and electromagnetic shielding properties, to the surfaces of various substrates, such as glass, ceramics, metals, and plastics; a structure having its surface covered with an electrically conductive film formed from the liquid; and a method for producing the liquid.

SOLUTION: A tetravalent titanium salt solution (e.g. a titanium tetrachloride solution) is reacted with a basic solution in the presence of an electroconductivity-improving substance (e.g. copper chloride, silver nitrate, or silica). The resultant hydroxide is peroxidized with an oxidizing agent (e.g. hydrogen peroxide) to form an amorphous-type titanium peroxide dispersion, which can be converted into an anatase type by further heating. Thus, a titanium oxide-containing conductive film-forming liquid comprising the dispersions of both types can be produced.

COPYRIGHT: (C)2002,JPO

JP2002-212463

English translation obtained at:

<http://www4.ipdl.inpit.go.jp/Tokujitu/PAJdetail.ipdl?N0000=60&N0120=01&N2001=2&N3001=2002-212463>

CLAIMS

[Claim(s)]

[Claim 1]Titanium oxide content conductive film formation liquid which consists of dispersion liquid containing quality of the choice goods for conductivity, and amorphous type titanium peroxide of a super-fine grain.

[Claim 2]The conductive film formation liquid according to claim 1 whose content of other ultrafine particles other than amorphous type titanium peroxide is 100 or less weight sections to amorphous type titanium peroxide 100 weight section.

[Claim 3]Titanium oxide content conductive film formation liquid which consists of dispersion liquid containing quality of the choice goods for conductivity, and anatase type titanium peroxide of a super-fine grain.

[Claim 4]The conductive film formation liquid according to claim 1, 2, or 3 with transparent dispersion liquid.

[Claim 5]quality of the choice goods for conductivity -- silica -- conductive film formation liquid given in any 1 of claims 1 thru/or 4 which are sol.

[Claim 6]A structure which has a conductive film containing quality of the choice goods for conductivity, and amorphous type titanium peroxide and/or anatase type titanium peroxide of a super-fine grain in a base surface.

[Claim 7]The structure according to claim 6 whose base is a translucency transparent substrate.

[Claim 8]The structure according to claim 6 or 7 in which a conductive film has a photocatalyst function or/and an antifouling function.

[Claim 9]The structure according to claim 6, 7, or 8 with transparent conductive film and base.

[Claim 10]Make salting in liquid and a basic solution of tetravalent titanium react, and hydroxide of titanium is formed, Carry out peroxidation of this hydroxide with an oxidizer, and this forms amorphous type titanium peroxide of a super-fine grain, And a manufacturing method of titanium oxide content conductive film formation liquid which consists of forming dispersion liquid which add quality of the choice goods for conductivity in either of this process, and contain quality of the choice goods for conductivity, and amorphous type titanium peroxide of a super-fine grain.

[Claim 11]Make salting in liquid and a basic solution of tetravalent titanium react, and hydroxide of titanium is formed, Carry out peroxidation of this hydroxide with an oxidizer, and also transfer anatase type titanium peroxide by heat-treating, and quality of the choice goods for conductivity is added in either of this process, A manufacturing method of titanium oxide content conductive film formation liquid which consists of forming dispersion liquid containing quality of the choice goods for conductivity, and anatase type titanium peroxide of a super-fine grain.

[Claim 12]A manufacturing method of the conductive film formation liquid according to claim 10 or 11 in which quality of the choice goods for conductivity is intermingled in reaction time of salting in liquid of tetravalent titanium, and a basic solution.

[Claim 13]A manufacturing method of titanium oxide content conductive film formation liquid which forms dispersion liquid which mix the dispersion liquid according to claim 10 and the dispersion liquid according to claim 11, and contain amorphous type titanium peroxide and anatase type titanium peroxide.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention Ceramics, such as sheet glass and a tile, a metal plate, a plastic sheet, To a various substrate or structure surfaces, such as a tank and a tank for admiration, photocatalyst performance, antibacterial performance, It is related with the manufacturing method of the structure which has the titanium oxide content conductive film formation liquid for forming the thin film which makes the outstanding function of various kinds, such as antifouling performance, antifog performance, antistatic performances, and electromagnetic shielding nature, reveal, and this conductive film in a base surface, and this conductive film formation liquid.

[0002]Especially this invention can make conductivity more specifically improve, It is related with the manufacturing method of the structure which has the titanium oxide content conductive film formation liquid for forming the protective film or functional membrane which can make a previous various function improve more as a result, and this conductive film in a base surface, and this conductive film formation liquid. It is related with the manufacturing method of the structure which has titanium oxide content conductive film formation liquid which can provide a protective film or functional membrane excellent in especially transparency, and this conductive film in a base surface, and this conductive film formation liquid.

[0003]

[Description of the Prior Art]The quality of a titanium inclusion is applied to various material-list sides, such as building materials, such as sheet glass, a white porcelain machine, a metal plate, or a tile, Forming the tunic which consists of titanium oxide (titania) which has various performances, such as base surface protective films, such as prevention from surface contamination, photocatalyst membrane, a dielectric film, semiconductor membrane, an ultraviolet-rays cut film, and a coloring coating film, is performed from old.

[0004]After applying the dispersion liquid or the titanium compound solution containing the particles of titanium oxide to a base surface and applying it as a formation method of the titanium oxide film, methods, such as desiccation or carrying out low temperature baking if needed further, are known. For example, there is the method of calcinating, after carrying out spreading desiccation of the method and titanium alkoxide which carry out spreading desiccation of the dispersion liquid produced from the titanium alkoxide by the sol gel process to the base surface directly.

[0005]In these methods, since acid and an organic substance were included, when

completing a coating film, it is required to heat to an elevated temperature and to remove these organic substances, and the obtained tunic had the problem of being easy to become heterogeneity or a porous membrane. When the dispersion liquid produced from the solution of the titanium-containing compound were also neglected at ordinary temperature, gelling and the condensation of particles took place from several hours in several days, and stability was very bad.

[0006]And in these methods, the material which can be applied since acid is included was restricted and there was also a problem which generates a harmful halogenated compound in the stage of calcination. Calcination temperature needed hundreds of times or more for forming a film good [adhesion] and precise, and use into materials, such as a plastic, metal, low melting glass, or building materials, had restrictions. Then, in order to solve such a problem, the paint for film formation which contained peroxypolytitanic acid in water etc. in the state where it dissolved or distributed, as a matrix component in which it is stable and calcination is simple was proposed (refer to JP,7-286114,A).

[0007]A comparatively high-density crystalline titania film is producible at low temperature, Preservation stability, hazardous property [as opposed to / it is good and / a builder], and the low paint for film formation are proposed (refer to JP,9-71418,A), The paint makes the titanium oxide particles which heat-treat in not less than 80 **, and consist of anatases generate, after making hydrogen peroxide solution act on hydroxylation titania gel. This paint is made useful into the coating material to the material [carry out / at low temperature / film formation] which cannot be heat-treated.

[0008]Although the paint in which the former was proposed contains peroxopolytitanic acid as a matrix component in the state or the state where it distributed dissolved in water etc., The titanium compound in the tunic formed with this coating liquid is not anatase type titanium oxide, and the manifestation of photocatalyst activity ability cannot be expected.

Since it was such, the coating liquid which makes it a solution technical problem for the titanium compound after film formation to be anatase type titanium oxide excellent in catalytic activity was also proposed (JP,10-67516,A).

[0009]This proposed liniment liquid has the good dispersion stability in a fluid besides said catalytic activity, and the desiccation after spreading and a baking process are easy for it, and it makes it a solution technical problem for the formed tunic to be also precise. The coating liquid is heated and prepared, after adding a peroxide in the liquid which distributed underwater titanium hydroxide or titanium oxide formed by the precipitation reaction from the titanium content fluid and making it a peroxotitanium solution. The surface of titanium oxide of an anatase type [solution / which was formed] was embellished with the peroxo group.

[0010]Since the titanium oxide content tunic mentioned above and its solution for film formation have various kinds of characteristics as mentioned above, there is a proposal besides said and, also after that, development of this solution for film formation and its pertinent art is furthered.

There are also various kinds of proposals accompanying them.

For example, there is a proposal (JP,9-262481,A) which provides the photocatalyst composition which carries out support immobilization of the photocatalyst grains on a

base by using amorphous type titanium peroxide sol as a binder.

[0011]Amorphous type titanium oxide, especially amorphous type titanium peroxide sol have high coupling nature, And having various functions, such as weatherability, electromagnetic wave interception nature, resistance to chemicals, static electricity ***** , and insect control nature, is found out, The proposal which provides the highly efficient nature coating agent which has these functions (JP,10-237352,A), Or there is also a proposal which makes the coating layer of amorphous type titanium peroxide sol combine with high adhesiveness also to the water-repellent surface (JP,10-53437,A), and it is dried and calcinated less than [ordinary temperature -250 **] after coating amorphous type titanium peroxide sol.

[0012]

[Problem(s) to be Solved by the Invention]Although such a titanium oxide content tunic is a highly efficient nature thing which has the various characteristics, in the actual condition, the functional expression in optical absence of antifouling performance and antifog performance is not enough. Also about the conductivity called for by an electromagnetic wave shield or ***** , it is not enough and the further improvement is desired about these characteristics. It excels in transparency from a point of fanciness and vision performance simultaneously with it, and a thing of high coupling nature is desired.

[0013]Paying attention to the highly efficient nature which titanium oxide especially a titanium peroxide content tunic, and this coating liquid for film formation have, and construction simple nature, this invention person is also striving for research and development wholeheartedly from old, and has proposed many results already developed as a result. Also after that, it continues, and the invention of the proposal is furthering research and development wholeheartedly, as a result, succeeded in development this time, and it was able to solve the problem which this mentioned above.

[0014]Therefore, this invention has electromagnetic wave shielding or the suitable conductivity for antistatic property with the outstanding antifouling performance and antifog performance, . The tunic of the high coupling nature which has the transparency which can reveal the fanciness and vision performance which are called for when forming in a windowpane etc. simultaneously can be provided. Let it be the issue which an invention should solve to provide the manufacturing method of the structure which has titanium content conductive film formation liquid and this conductive film in a base surface, and this conductive film formation liquid. That is, it sets it as the purpose of an invention to provide those things.

[0015]

[Means for Solving the Problem]In order that this invention may solve said technical problem, a structure which has titanium oxide content conductive film formation liquid, this formation liquid manufacturing method, and this conductive film in a base surface is provided. Titanium oxide content conductive film formation liquid of them is two sorts, a thing of dispersion liquid which contain amorphous type titanium peroxide fundamentally, and a dispersion-liquid thing containing anatase type titanium peroxide. Although it is as above, it is also possible by mixing both dispersion liquid to form that in which both an amorphous type and an anatase type are intermingled.

[0016]Conductive film formation liquid which consists of dispersion liquid containing the former amorphous type titanium peroxide, Conductive film formation liquid which

consists of dispersion liquid which contain quality of the choice goods for conductivity and amorphous type titanium peroxide of a super-fine grain, and contain the latter anatase type titanium peroxide contains quality of the choice goods for conductivity, and anatase type titanium peroxide of a super-fine grain.

[0017]When amorphous type titanium peroxide is contained also about a manufacturing method of the titanium oxide content conductive film formation liquid, Differ by a case where anatase type titanium peroxide is contained, and a manufacturing method of the former conductive film formation liquid, Make salting in liquid and a basic solution of tetravalent titanium react, and hydroxide of titanium is formed, It consists of carrying out peroxidation of this hydroxide with an oxidizer, and this forming amorphous type titanium peroxide, and forming dispersion liquid which add quality of the choice goods for conductivity in either of this process, and contain quality of the choice goods for conductivity, and amorphous type titanium peroxide of a super-fine grain.

[0018]By a manufacturing method of conductive film formation liquid of the latter which remains making salting in liquid and a basic solution of tetravalent titanium react, forming hydroxide of titanium, and carrying out peroxidation of this hydroxide with an oxidizer, and also heat-treating, It consists of making it transfer to anatase type titanium peroxide, adding quality of the choice goods for conductivity in either of this process, and forming dispersion liquid containing quality of the choice goods for conductivity, and anatase type titanium peroxide of a super-fine grain.

[0019]A structure which has a conductive film in a base surface has a conductive film containing quality of the choice goods for conductivity, and amorphous type titanium peroxide or anatase type titanium peroxide of a super-fine grain in a base surface. To a conductive film in that case, either one of amorphous type titanium peroxide or anatase type titanium peroxide may be independent, or any of coexistence of both may be sufficient.

[0020]And in this invention, a tunic which has the conductivity superior to an old solution for titanium oxide content film formation with titanium oxide content conductive film formation liquid can be formed on a base. Titanium oxide content conductive film formation liquid which consists of dispersion liquid containing amorphous type titanium peroxide of them is transparent, and can form in a base a tunic which has usable and good joint performance not only to a hydrophilic radical board but to a hydrophobic radical board. However, a formed tunic is hydrophobicity and there is no photocatalyst ability of a titania. Therefore, a base by which film formation was carried out has the special feature that degradation by a photocatalyst is avoidable.

[0021]Titanium oxide content conductive film formation liquid which consists of dispersion liquid containing anatase type titanium peroxide is transparent, and forms a tunic of hydrophilic nature. The formed tunic has catalyst ability, and is excellent in stability and has firm associative strength. Therefore, it is suitable especially when using it for a base which can form a tunic excellent in transparency and can ask for vision performances, such as a windowpane, as a result, while it has conductivity, antifouling performance, and antifog performance.

[0022]

[Embodiment of the Invention]This invention is titanium oxide content film formation liquid, this formation liquid manufacturing method, and a titanium oxide content tunic an invention of the structure which it has as it was mentioned above, and titanium oxide

content film formation liquid, Are two sorts, the thing of amorphous type titanium peroxide content, and the thing of anatase type titanium peroxide content, fundamentally, and the former, It is manufactured by making the salting in liquid and the basic solution of tetravalent titanium react, forming hydroxide of titanium, carrying out peroxidation of this hydroxide with oxidizers, such as hydrogen peroxide, and forming amorphous type titanium peroxide, and adding the quality of the choice goods for conductivity in either of this process.

[0023]The titanium oxide content film formation liquid containing the latter anatase type titanium peroxide, By making the salting in liquid and the basic solution of tetravalent titanium react, forming hydroxide of titanium, and carrying out peroxidation of this hydroxide with an oxidizer, and also heat-treating, it is made to transfer to anatase type titanium peroxide, and is manufactured by adding the quality of the choice goods for conductivity in either of this process. Although the number of the titanium oxide content film formation liquid of this invention as described above is two fundamentally, By mixing both dispersion liquid, it is also possible to form that in which both an amorphous type and an anatase type are intermingled, and when the mixing ratio adjusts, the ratio of the amorphous type of various ratios and an anatase type can be chosen freely.

[0024]As salting in liquid of the tetravalent titanium used in the case of titanium oxide content film formation liquid manufacture of this invention, If the gel of the titanium hydroxide called alt.titanic acid (H_4TiO_4) can be formed when it is made to react to basic solutions, such as an ammonia solution and a caustic-alkali-of-sodium solution, various kinds of titanium compounds can be used, There is a water-soluble inorganic acid salt of titanium, such as a titanium tetrachloride, titanium sulfate, nitric acid titanium, or titanium phosphate, in it. Water-soluble-organic-acids salts, such as a titanous oxalate, can also be illustrated besides it. A titanium tetrachloride is preferred at the point that any ingredients other than titanium in a titanium compound do not remain in the manufactured film formation liquid in these various titanium compounds.

[0025]The basic solution made to react to the salting in liquid of these tetravalent titanium, If it reacts to the salting in liquid of tetravalent titanium and the gel of titanium hydroxide can be formed, it is usable in various kinds of things, and an ammonia solution is preferred although an ammonia solution, a caustic-alkali-of-sodium solution, a sodium carbonate solution, or a caustic potash solution can be illustrated to it. If an after-oxidation peroxidation thing can form the titanium hydroxide formed after that as an oxidizer which oxidizes, various kinds of oxidizers can use it without restriction, but the hydrogen peroxide which residues, such as a metal ion or acid ion, do not produce in the manufactured film formation liquid is desirable.

[0026]About the concentration of the salting in liquid of tetravalent titanium, and both the solutions of a basic solution, especially if the concentration of reaction time is a range which can form the gel of titanium hydroxide, although it is not restricted, a comparatively thin solution is good. 5 - 0.01wt% of a tetravalent titanium salt solution is good, and, specifically, preferably [0.9 - 0.3wt% of] good. 10 - 0.5wt% of a basic solution is good, and preferably [4.0 - 2.0wt% of] good. 10 - 0.5wt% of the above mentioned range of the concentration at the time of using ammonia especially for a basic solution is good, and it is preferably [4.0 - 2.0wt% of] good.

[0027]If it can compare with the tunic formed with the film formation liquid of titanium oxide independent content as quality of the choice goods for conductivity and

conductivity can be made to improve, it is usable in various substances, such as metal salt. As metal salt, for example Aluminum, tin, chromium, nickel, antimony, There is metal salt, such as iron, silver, caesium, indium, cerium, selenium, copper, manganese, calcium, platinum, tungsten, a zirconium, and zinc, and it is usable also in hydroxide or an oxide about some of metal or nonmetals etc. besides it.

[0028]When a substance name shows more concretely about them, an aluminium chloride, the 1st and 2nd tin of chloridation, Chromium chloride, nickel chloride, the 1st and 2nd antimony of chloridation, the 1st and 2nd iron of chloridation, Silver nitrate, a cesium chloride, the indium 111 trichloride, the 1st cerium of chloridation, selenium tetrachloride, Various kinds of metal salt, such as cupric chloride, a manganese chloride, a calcium chloride, the 2nd platinum of chloridation, tungsten tetrachloride, oxytungsten dichloride, tungstic acid potassium, the 2nd carat of chloridation, zirconium oxychloride, and zinc chloride, can be illustrated. moreover -- as compounds other than metal salt -- hydroxylation indium, a tungstosilicic acid, and silica -- sol, calcium hydroxide, etc. can be illustrated.

[0029]In manufacture of the conductive film formation liquid of this invention, first, the salting in liquid and the basic solution of tetravalent titanium will be made to react, and titanium hydroxide gel will be formed. Although not necessarily limited especially for the concentration and temperature of reaction mixture in that case, it is preferred to carry out at a diluted solution and ordinary temperature. This reaction is a neutralization reaction and it is desirable to carry out until it can check to become neutrality, i.e., pH 7, from acidity. As for after the reaction, it is preferred to carry out solid liquid separation of the formed titanium hydroxide gel by weight sedimentation or centrifugal separation, and to rinse the after-separation said gel.

[0030]As for the quality of the choice goods for the conductivity used by this invention, it is desirable to make it live together, when making the salting in liquid and the basic solution of tetravalent titanium react and forming titanium hydroxide, and it is preferred to make it exist by addition etc. in the salting in liquid of tetravalent titanium before a hydroxide formation reaction for that purpose, or to add to the system of reaction at this reaction time. By doing in this way, depending on the quality of the choice goods for the conductivity added, hydroxide as well as titanium hydroxide is formed in hydroxide formation reaction time, and it can coprecipitate.

[0031]When the titanium hydroxide produced by making it above adds and carries out peroxidation of the oxidizers, such as hydrogen peroxide, to it, the amorphous type titanium peroxide of a super-fine grain which has conductivity is formed. The particle diameter of the particle is 2 nm - 20 nm, and when it is film formation liquid of the state where it is highly transparent and it is more preferred, it is 10 nm or less. The tunic formed with the conductive film formation liquid containing the obtained amorphous type titanium peroxide is hydrophobicity, and can form the tunic which was excellent not only in the base of hydrophilic nature but the hydrophobic radical object at fixing force.

[0032]There is no catalyst performance in the tunic formed, therefore the oxidation degradation of the base by light can be avoided. In the formation liquid, as for the ratio of the content of amorphous type titanium peroxide and the other super-fine grain, it is desirable that they are 100 or less weight sections to amorphous type titanium peroxide 100 weight section, and the conductive film formation liquid stable by this for hydrophobic film formation is obtained.

[0033]On the other hand, although the conductive film formation liquid containing anatase type titanium peroxide is formed by heating the amorphous type titanium peroxide solution of a super-fine grain formed above, 80-200 °C is good, the cooking temperature has especially simple heating under atmospheric pressure, and is preferred, the film formation liquid produced by doing in this way has high transparency, and the tunic formed as a result is highly transparent, and is suitable for the use which can ask for field-of-view performance or ornament performance. Hydrophilic nature is presented even in a dark place.

[0034]In manufacturing the titanium oxide content conductive film formation liquid which consists of dispersion liquid containing especially anatase type titanium peroxide, Both make a conductive improvement compound and the salting in liquid of tetravalent titanium coprecipitate as hydroxide in reaction time with a basic solution, The high dispersion liquid of transparency can be formed by oxidizing, carrying out peroxidation of the titanium oxide after that, heating subsequently, and making it transfer to an anatase type, It is suitable for translucency transparent substrates, such as the windowpane and optical glass of the building in which can form the high hydrophilic coating of transparency when a conductive film is formed using this, and importance is attached to field-of-view performance or fanciness as a result, or a plastic sheet.

[0035]Below, the embodiment of the manufacturing method of the conductive film formation liquid of this invention is described more focusing on a desirable mode at details based on a drawing. The conductive film formation liquid of this invention has what contains amorphous type titanium peroxide fundamentally, and two sorts of things containing anatase type titanium peroxide as it was mentioned above, but it is first explained based on drawing 1 from the manufacturing method of the former conductive film formation liquid.

[0036]In manufacturing the thing containing the former amorphous type titanium peroxide, a high-concentration titanium tetrachloride solution and ammonia solution are diluted first. Dilution is good to make it become 0.7 to 0.3 % of the weight, and 4.0 to 2.0% of the weight, respectively often [carrying out so that the concentration after dilution may be 5.0 to 0.01 % of the weight, and 10.0 to 0.5% of the weight, respectively], and preferably.

[0037]Although after-dilution both solutions are mixed and titanium hydroxide gel is formed, it is good for the reaction time for the quality of the choice goods for conductivity to live together in the system of reaction, therefore before performing said mixing, it is good in a titanium tetrachloride solution to mix the quality of the choice goods for conductivity. The quality of the choice goods for conductivity can use various kinds of things as it described above, but a copper chloride, the 1st and 2nd chloridation tin, or the 1st and 2nd ferric chloride is preferably good. When are described above and the quality of the choice goods for conductivity is made to mix, depending on the quality of the choice goods for the conductivity mixed, hydroxide as well as titanium hydroxide is formed in hydroxide formation reaction time, and it can coprecipitate.

[0038]Although not necessarily limited especially for the degree of reaction liquid temperature of a titanium oxide formation reaction, it is preferred to carry out at ordinary temperature. This reaction is a neutralization reaction and it is desirable to carry out to the grade which can check to become neutrality, i.e., pH 7, from acidity. As for after the reaction, it is preferred to rinse in order to remove negative ion, such as a chloride ion

which carry out solid liquid separation of the formed titanium hydroxide gel by gravity settling or centrifugal separation, and lives together from the after-separation said gel. [0039]Subsequently, although peroxidation of the titanium oxide will be carried out with an oxidizer, cooling before that is preferred. Cooling in that case is good to carry out so that titanium hydroxide may be 1-5 **. As an oxidizer at the time of carrying out peroxidation, hydrogen peroxide is desirable, and although the concentration in particular is not restricted, 30 to 40% of thing is good. About an oxidizer, it is not restricted to hydrogen peroxide, and if a peroxidation thing, i.e., titanium peroxide, can be formed as mentioned above, various kinds of things can be used.

[0040]Although a peroxidation reaction advances gradually and amorphous type titanium peroxide is formed by mixing titanium oxide and hydrogen peroxide as mentioned above, particle diameter is small, and in order to obtain the dispersion liquid which were excellent in transparency, it is good for low temperature to perform said reaction for a short time. The obtained dispersion liquid are the conductive film formation liquid as used in the field of this invention, by performing an ultrafiltration to this, moisture can be separated and concentration can be raised. Although the obtained film formation liquid is usually yellow, it receives the influence depending on the quality of the choice goods for the used conductivity, and becomes things, such as green or blue. In order to obtain the dispersion liquid which were excellent in transparency, when about 2 nm - 20 nm are good and is 10 nm or less, the particle diameter of a super-fine grain becomes what has high transparency, and is desirable.

[0041]As above-mentioned, the tunic obtained from the film formation liquid which consists of these amorphous type titanium peroxide content dispersion liquid is hydrophobicity, and, as a result, can form the tunic of strong fixing force not only in a hydrophilic radical object but in a hydrophobic radical object. There is no catalyst performance in the tunic, therefore the oxidation degradation of the base by light can be avoided. In the formation liquid, as for the ratio of the content of amorphous type titanium peroxide and the other ultrafine particle, it is desirable that they are 100 or less weight sections to amorphous type titanium peroxide 100 weight section, and the conductive film formation liquid stable by this for hydrophobic film formation is obtained.

[0042]Although the above is about the manufacturing method of the film formation liquid containing amorphous type titanium peroxide, the manufacturing method of the conductive film formation liquid which contains anatase type titanium peroxide below is explained. By heating the aforementioned amorphous type titanium peroxide dispersion liquid, titanium peroxide transfers to an anatase type from an amorphous type, anatase type titanium peroxide dispersion liquid are formed, and the conductive film formation liquid which, as a result, contains anatase type titanium peroxide can be manufactured. 80-200 ** of the cooking temperature in that case may be sufficient, and its 90-120 ** is preferably good. The heating is good to use heating by electromagnetic waves together to these, and to shorten cooking time as much as possible, although it is also possible to be based on the electrical and electric equipment or combustion heat.

[0043]The transparent dispersion liquid which transition from an amorphous type to an anatase type can be shortened when said concomitant use heating is adopted, and can control growth and condensation of the particle diameter of a super-fine grain, and do not weaken reduction of a peri oxo group and repulsive force (zeta-potential) with H₂O are

made. Thus, as for the particle diameter of a super-fine grain of the anatase type titanium peroxide obtained, 2-20 nm is good, and its 10 nm or less is desirably good. Although an amorphous type and two sorts of dispersion liquid of anatase type titanium peroxide can manufacture with the above-mentioned manufacturing method, respectively, it not only can use it alone, but both can form the dispersion liquid of arbitrary ratios by mixing both dispersion liquid.

[0044]About the addition stage of the quality of the choice goods for conductivity in the manufacturing method of the titanium oxide content conductive film formation liquid of this invention. The reaction front stirrup of the salting in liquid of tetravalent titanium, such as titanium tetrachloride, and a basic solution has preferred reaction time as above-mentioned, and it is also as above-mentioned that the thing outstanding about the various characteristics, such as transparency, conductivity, and a sticking tendency, by this is obtained. However, even if it mixes the quality of the choice goods for conductivity at the other stage of said manufacturing process, conductive film formation liquid can be manufactured, As the mixing stage, there are the time of the concentration adjustment film formation liquid manufacture after the ultrafiltration performed after the time of the concentration adjustment film formation liquid manufacture after the ultrafiltration performed after a peroxidation reaction or anatase type transition, etc. at the time of the sediment gel formation after the solid liquid separation before rinsing.

[0045]As a use subject of the conductive film formation liquid of this invention, the various materials or the structure in which various functions, such as photocatalyst performance, antibacterial performance, antifouling performance, antifog performance, antistatic ability, and electromagnetic shielding nature, are demanded corresponds. As these materials, plastic sheets, such as metal plates, such as sheet glass, ceramics, stainless steel, and aluminum, an acrylic, polycarbonate, and PET, a cheesecloth, textiles, etc. can be illustrated.

[0046]As a structure, vehicles sheathing materials, such as windowpanes, such as a building and a car, and a car, Various things, such as semiconductor materials, such as pipes, such as various tanks a tank, for admiration, etc., metal, and a plastic, sanitary chinaware, glasses, a lens, a lens filter, a hot-water-storing machine, organ bath apparatus, toilet apparatus, a sink, a door handle, a stopper cock for waterworks, a mirror for roads, an electromagnetic shielding material, and a substrate, and a copying machine inner component, can be illustrated.

[0047]The tunic formed with the film formation liquid of this invention, It excels in conductivity as mentioned above, and also in the case where a tunic is formed in pipe inner surfaces which photocatalyst ability cannot demonstrate easily as a result, such as metal and a plastic, contaminants, such as elasticity or a hard scale, slime, or iron rust, form, or do not adhere to a pipe inner surface easily, and it excels in the antifouling performance. When it is used especially for a water pipe, it is hard to generate a scale, slime, or ****, and suitable.

[0048]Besides, in addition, although there is no photocatalyst ability in a formation tunic therefore, when a base is a plastic, in particular in the case of the film formation liquid of amorphous type titanium peroxide dispersion liquid, there is also no anxiety of decomposition by sunlight on the contrary, and it becomes special feature. In the case of the film formation liquid of the dispersion liquid of anatase type titanium peroxide, Since a formation tunic is excellent in endurance and unity and transparency is also excellent,

in the case of transparent plastic plates, such as a windowpane or an acrylic, polycarbonate, and PET, or a container, it excels in the vision performance and antifouling performance and the antifog performance are also excellent.

[0049]

[Example] The example about manufacture of the conductive film which uses manufacture of the film formation liquid of this invention and this formation liquid for below is indicated. Although conductive examination, hydrophilic examination, and antifouling system performance testing are done about the tunic doubled and formed and those procedures and a result are indicated, It cannot be overemphasized that it is what this invention is not limited at all by these examples and examinations, and is specified by the statement of a claim. It is related with a film formation liquid manufacture example and a conductive film manufacture example, and the example of manufacture and the example of film formation are called below, respectively.

[0050][Example 1 of manufacture] The solution which added 10 g of titanium tetrachloride solutions (made by Sumitomo Sitix Corp.) in the solution which melted thoroughly purity 97% CuCl_2 and $2\text{H}_2\text{O}$ (made by Nihon Kagaku Sangyo Co., Ltd.) 0.463g in 500 ml of pure water 50 more%, added pure water to it, and was 1000 ml is prepared. The ammonia solution which diluted the ammonia solution (product made from Takasugi Pharmaceuticals) 10 times 25% was dropped at this, the pH to 6.9 was adjusted, and the mixture of copper hydroxide and titanium hydroxide was settled.

[0051] Washing was continued until the conductivity in supernatant liquid became 0.8 or less mS/m with pure water about this sediment, and after ending washing in the place where conductivity became 0.782 mS/m, 350g of content liquid of hydroxide of 0.96wt% concentration was produced. Subsequently, when 25g of hydrogen peroxide (product made from TAIKI Pharmaceutical industry) was added 35% and it stirred for 16 hours, cooling this content liquid at 1-5 **, the dispersion liquid 370g of the amorphous type titanium peroxide of 0.96wt% concentration in which transparent copper of blue-green was doped were obtained.

[0052] When 100g weighing of these obtained amorphous type titanium peroxide dispersion liquid was carried out and they were heated at 100 ** for 5 hours, the anatase type titanium peroxide dispersion liquid 60g of 1.6wt% concentration were obtained for the anatase type titanium peroxide sol which blueness increases further and by which copper of strong blue-green was doped. This was diluted with pure water and it prepared to the 0.85wt% anatase type titanium peroxide dispersion liquid 112g for film formation spreading. The dispersion liquid 270g of the remaining amorphous type titanium peroxide were diluted with pure water, and prepared the dispersion liquid 304g of 0.85wt% of amorphous type titanium peroxide.

[0053][Example 2 of manufacture] To 0.85wt% of the anatase type titanium peroxide dispersion liquid 60g in the example of comparison manufacture which carries out a postscript, 0.050g of silver nitrate was added so that it might become concentration 0.005 mol/l, and the anatase type titanium peroxide dispersion liquid in which silver was doped were prepared.

[0054][Example 3 of manufacture] To the dispersion liquid 67g of 0.85wt% of the anatase type titanium peroxide in which the copper prepared in said example 1 of manufacture was doped, 0.057g of silver nitrate was added so that it might become concentration 0.005 mol/l, and the dispersion liquid of the anatase type titanium peroxide

in which silver and copper were doped were prepared.

[0055][Example 4 of manufacture] In the solution which melted thoroughly purity 97% CuCl_2 and $2\text{H}_2\text{O}$ (made by Nihon Kagaku Sangyo Co., Ltd.) 0.463g in the pure water 500g. further -- 30wt% silica -- the solution which added 2.5 g of sol and 10 g of 50wt% titanium tetrachloride solutions (made by Sumitomo Sitix Corp.), added pure water, and was 1000 g is prepared. The ammonia solution which diluted the ammonia solution (product made from Takasugi Pharmaceuticals) 10 times 25% was dropped at this, the pH to 6.9 was adjusted, and the mixture of copper hydroxide and titanium hydroxide was settled.

[0056] Washing was continued until the conductivity in supernatant liquid became 0.8 or less mS/m with pure water about this sediment, and after ending washing in the place where conductivity became 0.688 mS/m, 345g of content liquid of hydroxide of 0.96wt% concentration was produced. Subsequently, when 25g of hydrogen peroxide (product made from TAIKI Pharmaceutical industry) was added 35% and it stirred for 16 hours, cooling this content liquid at 1-5 **, the dispersion liquid 370g of the amorphous type titanium peroxide of 1.05wt% concentration in which transparent copper and silica of blue-green were doped were obtained.

[0057] These obtained amorphous type titanium peroxide dispersion liquid. When 100g weighing was carried out and it heated at 100 ** for 5 hours, 60g of anatase type titanium peroxide sol by which copper, copper in which the strong copper rust color of blueness is more transparent than the dispersion liquid of the amorphous type titanium peroxide in which silica was doped, and silica were doped was obtained by 1.72wt% concentration. This was diluted with pure water and it prepared to the 0.85wt% anatase type titanium peroxide dispersion liquid 120g for film formation spreading.

[0058][Example of comparison manufacture] The solution which added 10 g of 50wt% titanium tetrachloride solutions (made by Sumitomo Sitix Corp.) to the pure water 500g, added pure water, and was 1000 g is prepared. The ammonia solution which diluted the ammonia solution (product made from Takasugi Pharmaceuticals) 10 times 25% was dropped at this, the pH to 6.9 was adjusted, and titanium hydroxide was settled. Washing was continued until the conductivity in supernatant liquid became 0.8 or less mS/m with pure water about this sediment, and after ending washing in the place where conductivity became 0.738 mS/m, 430g of content liquid of hydroxide of 0.73wt% concentration was produced.

[0059] Subsequently, when 25g of hydrogen peroxide (product made from TAIKI Pharmaceutical industry) was added 35% and it stirred for 16 hours, cooling this content liquid at 1-5 **, the dispersion liquid 450g of amorphous type titanium peroxide of light-yellowish-brown-color 0.86wt% concentration were obtained. When 100g weighing of these obtained amorphous type titanium peroxide dispersion liquid was carried out and they were heated at 100 ** for 5 hours, 55g of light yellow anatase type titanium peroxide dispersion liquid were obtained by 1.52wt% concentration. This was diluted with pure water and it prepared to the 0.85wt% anatase type titanium peroxide dispersion liquid 98g for film formation spreading.

[0060][Example 5 of manufacture] The solution which added 10 g of titanium tetrachloride solutions (made by Sumitomo Sitix Corp.) in the solution which melted thoroughly FeCl_3 and $6\text{H}_2\text{O}$ (ferric chloride) 0.712g in 500 ml of pure water 50 more%, added pure water to it, and was 1000 ml is prepared. The ammonia solution which diluted

the ammonia solution (product made from Takasugi Pharmaceuticals) 10 times 25% was dropped at this, the pH to 7.1 was adjusted, and the mixture of iron hydroxide and titanium hydroxide was settled. Washing was continued until the conductivity in supernatant liquid became 0.8 or less mS/m with pure water about this sediment, and after ending washing in the place where conductivity became 0.744 mS/m, 420g of content liquid of hydroxide of 0.47wt% concentration was produced.

[0061]Subsequently, when 25g of hydrogen peroxide (product made from TAIKI Pharmaceutical industry) was added 35% and it stirred for 16 hours, cooling this content liquid at 1-5 **, the dispersion liquid 440g of the amorphous type titanium peroxide in which iron with a transparent dark yellowish brown color was doped were able to obtain. When 100g weighing of the obtained amorphous type titanium peroxide dispersion liquid was carried out and they were heated at 100 ** for 5 hours, the anatase type titanium peroxide dispersion liquid 48g of 1.1wt% concentration were obtained for the anatase type titanium peroxide sol by which light yellow iron was doped.

[0062][Example 6 of manufacture] The solution which added 10 g of titanium tetrachloride solutions (made by Sumitomo Sitix Corp.) in the solution which melted thoroughly SnCl_2 and $2\text{H}_2\text{O}$ (stannous chloride)0.594g in 500 ml of pure water 50 more%, added pure water to it, and was 1000 ml is prepared. The ammonia solution which diluted the ammonia solution (product made from Takasugi Pharmaceuticals) 10 times 25% was dropped at this, the pH to 7.0 was adjusted, and the mixture of hydroxylation tin and titanium hydroxide was settled. Washing was continued until the conductivity in supernatant liquid became 0.8 or less mS/m with pure water about this sediment, and after ending washing in the place where conductivity became 0.713 mS/m, 417g of content liquid of hydroxide of 0.51wt% concentration was produced.

[0063]Subsequently, when 25g of hydrogen peroxide (product made from TAIKI Pharmaceutical industry) was added 35% and it stirred for 16 hours, cooling this content liquid at 1-5 **, the dispersion liquid 439g of the amorphous type titanium peroxide in which tin with a transparent yellowish brown color was doped were able to obtain. When 100g weighing of the obtained amorphous type titanium peroxide dispersion liquid was carried out and they were heated at 100 ** for 5 hours, the anatase type titanium peroxide dispersion liquid 48g of 1.02wt% concentration were obtained for the anatase type titanium peroxide sol by which light yellow tin was doped.

[0064][Example 7 of manufacture] The solution which added 10 g of titanium tetrachloride solutions (made by Sumitomo Sitix Corp.) in the solution which melted ZnCl_2 (zinc chloride) 0.359g thoroughly in 500 ml of pure water 50 more%, added pure water to it, and was 1000 ml is prepared. The ammonia solution which diluted the ammonia solution (product made from Takasugi Pharmaceuticals) 10 times 25% was dropped at this, the pH to 7.0 was adjusted, and the mixture of zinc hydroxide and titanium hydroxide was settled. Washing was continued until the conductivity in supernatant liquid became 0.8 or less mS/m with pure water about this sediment, and after ending washing in the place where conductivity became 0.713 mS/m, 409g of content liquid of hydroxide of 0.48wt% concentration was produced.

[0065]Subsequently, when 25g of hydrogen peroxide (product made from TAIKI Pharmaceutical industry) was added 35% and it stirred for 16 hours, cooling this content liquid at 1-5 **, the dispersion liquid 430g of the amorphous type titanium peroxide in which zinc with a transparent yellowish brown color was doped were able to obtain.

When 100g weighing of the obtained amorphous type titanium peroxide dispersion liquid was carried out and they were heated at 100 °C for 5 hours, the anatase type titanium peroxide dispersion liquid 48g of 0.96wt% concentration were obtained for the anatase type titanium peroxide sol by which light yellow zinc was doped.

[0066][Example 8 of manufacture] The solution which added 10 g of titanium tetrachloride solutions (made by Sumitomo Sitix Corp.) in the solution which melted thoroughly NiCl_2 and $6\text{H}_2\text{O}$ (nickel chloride) 0.594g in 500 ml of pure water 50 more%, added pure water to it, and was 1000 ml is prepared. The ammonia solution which diluted the ammonia solution (product made from Takasugi Pharmaceuticals) 10 times 25% was dropped at this, the pH to 7.0 was adjusted, and the mixture of nickel hydroxide and titanium hydroxide was settled. Washing was continued until the conductivity in supernatant liquid became 0.8 or less mS/m with pure water about this sediment, and after ending washing in the place where conductivity became 0.679 mS/m, 403g of content liquid of hydroxide of 0.71wt% concentration was produced.

[0067]Subsequently, when 25g of hydrogen peroxide (product made from TAIKI Pharmaceutical industry) was added 35% and it stirred for 16 hours, cooling this content liquid at 1-5 °C, the dispersion liquid 425g of the amorphous type titanium peroxide in which nickel with a transparent dark yellowish brown color was doped were able to obtain. When 100g weighing of the obtained amorphous type titanium peroxide dispersion liquid was carried out and they were heated at 100 °C for 5 hours, the anatase type titanium peroxide dispersion liquid 48g of 1.30wt% concentration were obtained for the anatase type titanium peroxide sol by which light yellowish brown nickel was doped.

[0068][Example 9 of manufacture] in the solution which melted thoroughly purity 97% CuCl_2 and $2\text{H}_2\text{O}$ (made by Nihon Kagaku Sangyo Co., Ltd.) 0.230g, and FeCl_3 and $6\text{H}_2\text{O}$ (ferric chloride) 0.351g in 500 ml of pure water. The solution which added 10 g of titanium tetrachloride solutions (made by Sumitomo Sitix Corp.) 50 more%, added pure water, and was 1000 ml is prepared. The ammonia solution which diluted the ammonia solution (product made from Takasugi Pharmaceuticals) 10 times 25% was dropped at this, the pH to 7.0 was adjusted, and the mixture of copper hydroxide, iron hydroxide, and titanium hydroxide was settled. Washing was continued until the conductivity in supernatant liquid became 0.8 or less mS/m with pure water about this sediment, and after ending washing in the place where conductivity became 0.779 mS/m, 398g of content liquid of hydroxide of 0.76wt% concentration was produced.

[0069]Subsequently, when 25g of hydrogen peroxide (product made from TAIKI Pharmaceutical industry) was added 35% and it stirred for 16 hours, cooling this content liquid at 1-5 °C, the dispersion liquid 420g of the amorphous type titanium peroxide in which transparent copper and iron of blue-green were doped were able to obtain. When 100g weighing of the obtained amorphous type titanium peroxide dispersion liquid was carried out and they were heated at 100 °C for 5 hours, the anatase type titanium peroxide dispersion liquid 45g of 1.42wt% concentration were obtained for the anatase type titanium peroxide sol by which copper and iron of the copper rust color were doped.

[0070][The examples 1 thru/ or 4 of film formation and film formation comparative example] The coat was formed in the 10x10-cm porcelain tile surface using the dispersion liquid of the anatase type titanium peroxide manufactured in the amorphous type manufactured in the examples 1 and 4 of manufacture, and the example of comparison manufacture, and the examples 2 and 3 of manufacture. It heated for 15

minutes at 100 °C after coat formation, and the tile for conductivity and a hydrophilic examination was prepared.

[0071][Conductive examination] The surface resistance measuring apparatus (RORESUTA AP, Mitsubishi Chemical make) was used for conductivity, and it measured point to point surface resistance about the tile prepared above. When this measured value is low, excelling in conductivity is shown. Therefore, conductivity will be inferior when high.

[0072][Hydrophilic examination] The angle-of-contact meter (a CA-X type, the product made from Harmony Interface Science) was used for hydrophilic nature, and about the tile prepared above, after neglecting it in a dark place for after-adjustment 40 hours, it measured the hydrophilic angle in the procedure as follows. When this measured value is less than 10-40 degrees, it is hydrophilic nature, and in the case of 40-80 degrees, it is hydrophobicity.

[0073]These measurement result is as being shown in Table 1. According to this result, the surface resistance of the tile prepared using the titanium peroxide content dispersion liquid of the example of comparison manufacture in which the quality of the choice goods for conductivity is not mixed compares with it of the example of manufacture which is an example, and it turns out that triple or more figures surface resistance is large, and conductivity is low.

[0074]As for the case where titanium peroxide is an amorphous type, in the film formation liquid of this invention in which the quality of the choice goods for conductivity was mixed, the direction in anatase type also shows excelling in conductivity from this table. About the quality of the choice goods for the conductivity to mix, a direction in case silica is intermingled rather than the case of only metallic compounds also understands excelling in conductivity.

[0075]And about hydrophilic nature, in the case of the tunic by anatase type dispersion liquid, the direction in the case of the tunic by amorphous type dispersion liquid compares from Table 1 similarly, a hydrophilic angle is large, and it turns out that it is hydrophobicity. When especially the copper compound is mixed, it is the hydrophilic angle of this more than twice at the time of using the formation liquid of conductive improvement substance unmixed example of comparison manufacture.

It is super-hydrophilic nature.

When silica is mixing with metallic compounds as a conductive improvement compound, a hydrophilic angle is smaller than the case of only metallic compounds, and it is super-hydrophilic nature.

[0076]

[Table 1]

試験例番号	使用分散液	導電性 (Ω/\square)	親水性
被膜形成例 1	製造例 1 (アモルファス型)	4.0×10^4	85°
被膜形成例 2	製造例 2 (アナターズ型)	5.6×10^3	10°
被膜形成例 3	製造例 3 (アナターズ型)	3.2×10^3	8°
被膜形成例 4	製造例 4 (アモルファス型)	2.1×10^4	15°
被膜形成比較例	比較製造例 (アモルファス型)	3.0×10^7	42°

[0077][Antifouling quality assessment] The conductive film formation liquid for antifouling quality assessments was first prepared as follows.

[Example 10 of manufacture] 0.85wt% of the anatase type dispersion liquid 60g in which copper and silica in said example 4 of manufacture were doped are extracted, On the other hand, 0.050g of silver nitrate was added so that it might become 0.005 mol/l, and the anatase type titanium peroxide dispersion liquid in which copper, silver, and silica were doped were prepared.

[0078][Example 11 of manufacture] 0.85wt% of the amorphous type titanium peroxide dispersion liquid in which the copper obtained in the example 1 of manufacture was doped, and 0.85wt% of the anatase type titanium peroxide dispersion liquid in which copper was doped were mixed at a rate of 3:7, and 60g of mixed liquor was prepared. To this mixed liquor, 0.050g of silver nitrate was added so that it might become concentration 0.005 mol/l, and the titanium oxide content conductive film formation liquid in which copper and silver were doped was prepared.

[0079][Preparation of the sample for antifouling quality assessments] The titanium oxide content conductive film formation liquid which consists of dispersion liquid containing the anatase type titanium peroxide which was prepared in the example 10 of manufacture, and which mixes a silver compound, a copper compound, and silica 100 mm in inside diameter. Film formation was carried out to the inner surface of 200 mm in length a stainless steel pipe (SUS 304), it heated for 15 minutes at 250 °C after desiccation, and the conductive film was formed. The same stainless steel pipe that does not form conductive film formation liquid for comparison was also prepared (comparative example 1).

[0080]Spray spraying of the conductive film formation liquid prepared in the example 11 of manufacture was carried out at the acrylic resin plate (70x120 mm) so that the amount of coats might serve as 0.8 g/cm², and it heated for 15 minutes at 80 °C after desiccation, and the conductive film was formed. The same resin board that does not form conductive film formation liquid for comparison was also prepared (comparative example 2).

[0081][Antifouling system performance testing] The pipe and resin board which do not form the conductive film for comparison in addition to the pipe and the resin board, and it

which were manufactured above are put into a plastic container with a capacity (l) of 20 l. with 10 l. of river water, It saved in the dark place, it took out one month and two months afterward, and surface contamination status was observed visually. The result is as being shown in Table 2.

[0082][Contamination status valuation basis] The valuation basis of contamination status was evaluated with the dirt adhering to the surface as follows.

O : there is almost no adhesion.

** : There is adhesion a little.

x: Adhesion is clear.

[0083]The evaluation result of contamination status is as being shown in Table 2. As for the pipe and resin board of an example with which the conductive film is formed in the surface, according to the result, it is clear to compare with the thing of a comparative example in which it is not formed, and for there to be no adhesion of dirt, and to excel in antifouling property. Although a difference is in the quality of the choice goods for the mixed conductivity in part, about titanium peroxide, the direction in the case of an anatase type independent excels the case where the amorphous type and the anatase type are intermingled in the antifouling performance.

[0084]

[Table 2]

使用分散液	試験期間	
	1 ヶ月	2 ヶ月
製造例 10	○	○
比較例 1	△	×
製造例 11	○	△
比較例 2	△	×

[0085]

[Effect of the Invention]The titanium oxide content conductive film formation liquid of this invention can form the tunic which has the conductivity superior to the old solution for titanium oxide content film formation in various kinds of base surfaces, such as ceramics, such as sheet glass and a tile, a metal plate, and a plastic sheet. The outstanding function of various kinds, such as antistatic performances, such as antifouling performances, such as photocatalyst performance, antibacterial performance, a tile, or a glass surface, antifog performance, the copying machine inside of a plane, etc. which have deleterious material resolution, such as a microorganism, by this tunic, and electromagnetic shielding nature, can be made to reveal.

[0086]Especially, since especially conductivity can be made to improve, it can have good influence on the function relevant to it. For example, the ionized substance becomes difficult to adhere. The tunic formed from amorphous type titanium peroxide content dispersion liquid among the conductive film formation liquid which has such the characteristic does not have photocatalyst ability at hydrophobicity. Therefore, the tunic which has the unity excellent not only in a hydrophilic radical object but the hydrophobic radical object can be formed, and a film formation base has the special feature that

degradation by a photocatalyst is avoidable.

[0087]The titanium oxide content conductive film formation liquid which consists of anatase type titanium peroxide content dispersion liquid is transparent, and it is hydrophilic nature, and the formed tunic has photocatalyst ability, and is excellent also in stability and unity. Therefore, it is suitable when the tunic excellent in transparency uses it for the base which can form by stability and strong combination and can ask for vision performances, such as a windowpane, as a result, while it has conductivity, antifouling performance, and antifog performance.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]The figure showing the outline of the manufacturing method of the conductive film formation liquid of this invention.